

COATINGS. ENAMELS

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CERAMIC COATINGS FOR FUNCTIONALLY GRADED HIGH-TEMPERATURE HEAT-SHIELDING MATERIALS

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Ceramic coatings based on organosilicon polymers are studied. The physical-thermal and mechanical properties of heat-shielding material with and without a coating are analyzed. It is found that ceramic coatings can be used to increase the mechanical properties of functionally graded heat-shielding materials based on the system $\text{Al}_2\text{O}_3\text{--SiO}_2$.

Key words: ceramic coatings, polycarbosilanes, linear shrinkage, temperature resistance, modifying components.

To develop single- and multiuse advanced hypersonic aircraft (HSA) for aerospace applications it is necessary to solve a number of complicated problems taken as a whole. One such problem is to develop high-temperature heat-shielding materials.

Since HSA completing a long flight in the atmosphere is subjected to significant aerodynamic heating in the presence of a large velocity differential, the problem of developing heat-shielding material is defining. Heat-shielding materials must preserve relatively high strength, temperature resistance and minimal linear shrinkage in order to preserve the structural shape of parts.

The serviceability of heat-shielding materials (HSM) can be increased by using multifunctional coatings, which increase the temperature resistance and mechanical strength of HSM. The development of ceramic strengthening coatings (SC) capable of operating for a long time at temperatures to 1650°C and at the same time increasing the structural strength of HSM is a critical scientific and engineering problem.

The main requirements for the composition of strengthening coatings have been determined on the basis of theoretical and experimental studies: working temperature 1650°C, content of the critical phase ≥ 70 wt.%; 20 – 30% increase of the ultimate compression strength of functionally

graded fiber material with the thermophysical properties changing by $\leq 3\%$ ² [1 – 5].

Previous research on the synthesis of high-temperature thin-film coatings for inorganic fiber materials made it possible to determine the following:

- coating system – $\text{SiC--Si}_3\text{N}_4\text{--SiO}_2\text{--MoSi}_2$;
- method of obtaining a coating — pyrolytic decomposition of ceramic-forming polymer — polycarbosilane and polysiloxane in an inert medium.

To improve the protective and strengthening properties of coatings it is expedient to introduce modifying components containing ultradisperse, glass-forming, boron-containing and thermodynamically stable oxygen-free compounds.

The following initial components were chosen for experiments on the synthesis of SC: organosilicon polymer polycarbosilane PKS-21M, amorphous boron B_{am} and molybdenum disilicide MoSi_2 . Under certain conditions these components can enter into a chemical reaction in which a complex ceramic coating system is formed — $\text{SiC--Si}_3\text{N}_3\text{--SiO}_2\text{--MoSi}_2$. The following are necessary to achieve a higher degree of completion of the chemical reaction: high heating temperature, inert medium and maximum contact area of the reactants, which is achieved by providing a large specific surface area of the modifying filler particles.

The quality of the initial components and the properties of the functionally graded ceramic fiber material (GCFM) with SC were determined as follows: aggregate state of the

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² Here and below, content by weight, %.

substances — following GOST 20841; particle size — by the procedure contained in the instructions for the Analizette apparatus; the content of the solid phase of the polymer — following GOST 17537; moisture content of the powders — following GOST 9758; oxidizability of the solid phase of the strengthening coating — following GOST 6130; temperature resistance and linear shrinkage of GCFM with a SC — following GOST 17177; compression strength — following GOST 17177; and, thermal conductivity — following RTM 1.2.088.

The technological properties of the prepared samples of the strengthening-coating suspensions were studied — the viscosity and density of the suspensions, the solid phase content — and thermogravimetric tests of the solid phase of the coating were performed. Working solutions of the ceramic-forming polymer with concentrations 2–30% were used to obtain the suspensions. The preparation of the modifying components B_{am} and $MoSi_2$ included drying the components, grinding and mixing in a porcelain drum in a roller mill.

The suspensions of the strengthening coatings were prepared by combining the working solutions of the ceramic-forming polymer at different concentrations with the modifying fillers and followed by mechanical mixing of the mixture in a porcelain container for 10–15 min, after which the suspension was poured into a glass container with a hermetic top. In the course of determining the technological properties of the SC suspensions it was found that as the content of the modifying components and the concentration of the ceramic-forming polymer in the SC suspensions increased the following also increased: the solid phase content from 70 to 73%, conventional viscosity from 14 to 18 sec and density of the suspensions from 680 to 755 kg/m³.

Preliminary tests of the samples of SC and GCFM with SC for the oxidizability of the solid phase of SC, the temperature resistance and phase stability of GCFM with SC at the working temperature 1650°C and the mechanical strength showed that all the SC compositions studied possess elevated oxidation resistance at 1650°C for $\tau = 1$ h, the mass increase of the samples does not exceed 1%, the coatings give GCFM temperature resistance at 1650°C for 1 h and the minimum shrinkage is 0–1%.

Phase analysis of the diffraction patterns of GCFM with SC in the initial state and after heat-treatment shows that practically all are identical. The base phases are Al_2O_3 and mullite $2Al_2O_3 \cdot 3SiO_2$ for GCFM and SiC , Si_3N_4 , $MoSi_2$ and SiB_4 for SC. No crystalline phase of silicon carbide is observed in the diffraction patterns of GCFM with SC; this indicates phase stability of the strengthening coating, where silicon carbide is in the amorphous state.

TABLE 1. Tests Results for the Physical-Mechanical Properties of GCFM and GCFM + SC Samples

Sample No.	Experimental material	Number of SC layers	SC deposition method	Density, g/cm ³	σ_c ,* MPa	Compression strength increase, %
1	Uncoated GCFM	—	—	0.280	0.21	—
2	GCFM + SC 3% PKS solution	1	Permeation	0.284	0.27	35
3	GCFM + SC 3% PKS solution	2	Same	0.289	0.31	55
4	GCFM + SC 5% PKS solution	1	"	0.291	0.34	70
5	GCFM + SC 5% PKS solution	2	"	0.296	0.42	110
6	Uncoated GCFM	—	—	0.280	0.21	—
7	GCFM + SC 3% PKS solution	1	Brushing	0.303	0.38	31
8	GCFM + SC 3% PKS solution	2	Same	0.307	0.41	41
9	GCFM + SC 5% PKS solution	1	"	0.306	0.45	55
10	GCFM + SC 5% PKS solution	2	"	0.311	0.61	110

* σ_c) average compression strength, MPa.

Studies of the process conditions for SC deposition and formation on GCFM included determination of the following: the permeation time; drying regimes; consumption of suspensions during SC deposition; effect of the number of coating layers deposited on the physical-mechanical properties of GCFM; and, temperature-time regimes for coating formation. Two deposition methods were studied: 1) permeation and 2) brushing on.

The results were as follows:

- the permeation time of SC suspensions based on PKS-21M solutions into the GCFM + SC samples was the same and equal to 0.25–1 h; the sample mass changes by 8–15%;

- the drying time of GCFM + SC (permeation method): from 5 to 12 h for a single layer in air, from 2 to 3 h in a drying cabinet at 40°C, from 7 to 24 h for two layers in air, from 3 to 6 h in a drying cabinet at 40°C;

- the consumption of SC suspension per unit surface area of the GCFM (brushing on): SC based on PKS-21M solution per layer — 2.0–2.2 g/cm²; in two layers — 3.0–3.4 g/cm²;

- the drying time of GCFM + SC (brushing on): from 3 to 5 h in one layer in air, from 0.5 to 1.5 h in a drying cabinet at 40°C; from 6 to 15 h in two layers in air, from 1.5 to 4 h in a drying cabinet at 40°C;

- SC formation regime: permeation methods — $t = 1100^\circ C$, $\tau = 1$ h; brushing on — $t = 1100^\circ C$, $\tau = 0.5$ h.

The test results for the physical-mechanical properties of GCFM and GCFM + SC samples are presented in Table 1.

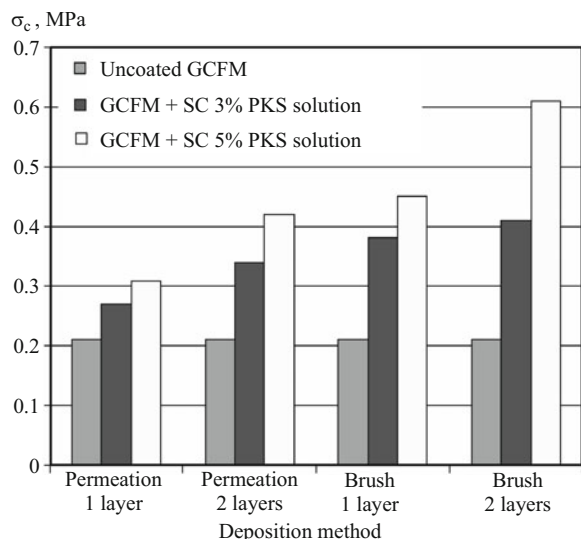


Fig. 1. Effect of the SC composition and deposition method on compression strength σ_c of GCFM.

The studies showed that the strengthening coating increased the mechanical strength of GCFM by 35 – 110%; the maximum strength 0.42 – 0.61 MPa was obtained for samples with a two-layer strengthening coating based on a 5% PKS solution. Both deposition methods increase the strength of GCFM identically (see Fig. 1).³

The thermal conductivity was studied for $100 \times 100 \times 5$ mm GCFM and GCFM + SC samples. Its value was 0.09 W/(m · K) in uncoated samples and 0.09 W/(m · K) in coated samples at 20°C, 0.35 W/(m · K) in uncoated samples and 0.31 W/(m · K) in coated samples at 1650°C (according to test specifications 0.35 – 0.40 W/(m · K)). Taking the measurement error to be 15 – 20% it can be assumed that the heat-insulation properties of GCFM do not change after coating deposition.

The new SC suspensions must meet the requirements presented in Table 2.

The composition and technology for obtaining a strengthening coating in the system $\text{SiC-Si}_3\text{N}_4\text{-SiO}_2\text{-MoSi}_2\text{-SiB}_4$ were developed for functionally graded ceramic fiber material.

The studies and optimal regimes chosen for deposition and formation of a strengthening coating on GCFM made it possible to obtain GCFM + SC samples with the density varying by no more than 4.9% relative to the initial material.

The determination of the temperature resistance of SC and GCFM + SC established the following:

- the composition of the solid phase of SC possesses enhanced oxidizability at 1650°C for 20 h, the weight increment of the samples does not exceed 2.9%;

TABLE 2. Requirements for the New SC Suspension

Parameter	Suspensions developed	
	SC No. 2	SC No. 5
Exterior view	Grey suspension	
Conventional viscosity, sec	12 – 13	13 – 14
Suspension density, g/cm ³	0.284	0.296
Ceramic phase content, %, not less than	78 – 80	

- the shrinkage of the GCFM + SC samples after heating at 1650°C over 2 h was 0 – 1%.

It was determined that the SC does not increase the GCFM shrinkage.

The phase composition of GCFM + SC in the initial state is: the base phase is mullite ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and $\alpha\text{-Al}_2\text{O}_3$ is partially present.

The phase composition of GCFM + SC after high-temperature tests (1650°C, 2 h) is: base phase mullite ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$); $\delta\text{-Al}_2\text{O}_3$, SiC, Si_3N_4 , MoSi_2 and SiB_4 are present.

Strengthening coatings can be used to prepare the heat-shielding elements of the combustion chamber of the fuel channel of an advanced gas-turbine engine as well as in the power and gas-oil-pumping facilities and transport systems as heat-insulating materials for the linings of high-temperature furnaces and other power-generating facilities.

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